

# Sputter Deposition of Silicon-Oxide Optical Coatings

*A. F. Jankowski, J. P. Hayes, T. E. Felter, C. Evans, A. J. Nelson*

This article was submitted to  
International Conference on Metallurgical Coatings and Thin Films,  
San Diego, CA., April 22-26, 2002

**March 22, 2002**

**U.S. Department of Energy**

Lawrence  
Livermore  
National  
Laboratory

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
And its contractors in paper from  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
Telephone: (865) 576-8401  
Facsimile: (865) 576-5728  
E-mail: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for the sale to the public from  
U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: (800) 553-6847  
Facsimile: (703) 605-6900  
E-mail: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory  
Technical Information Department's Digital Library  
<http://www.llnl.gov/tid/Library.html>

# **Sputter Deposition of Silicon-Oxide Optical Coatings**

A.F. Jankowski, J.P. Hayes, T.E. Felter, C. Evans, and A.J. Nelson

*Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550*

## **Abstract**

Fused silica and Si-O<sub>x</sub> coatings are of interest for use under high flux conditions of laser light. Si-O<sub>x</sub> coatings are sputter deposited from silicon and fused quartz targets using planar magnetrons operated in the rf mode with a variable working-gas mixture of Argon-Oxygen. A series of coatings are prepared on optically flat, fused quartz substrates. Analysis of surface curvature reveals the deposition process conditions that minimize residual stress. Compressive stress levels that exceed 1.5 GPa can be reduced to less than 0.4 GPa for an optimum working gas pressure. Characterization using Rutherford backscattering and x-ray photoelectron spectroscopy indicates that both the fused quartz and silicon targets can be used to sputter deposit coatings with the chemical bonding features of the fused-quartz substrate material.

## **Introduction**

A widely used practice to produce oxides for use as defect-free and hard optical coatings is the physical vapor deposition method of magnetron sputtering. In one application, this method may be an attractive alternative to polishing the surface of fused quartz to a high finish. The polishing process can leave a surface containing impurities or defects that become sites for damage when exposed to laser light at high fluence. Extensive cleaning procedures for the polished surfaces can be required prior to exposure to laser light in order to minimize damage. <sup>[1-2]</sup>

An alternative for the creation of a defect-free surface is through a coating procedure that produces

a surface compatible with the substrate and the exposure to laser light. At present, we investigate the use of reactive sputter deposition to produce Si-O<sub>x</sub> coatings that are compatible with a fused quartz substrate. The residual state-of-stress is an important consideration in producing mechanical stable coatings that do not alter the figure of the optic. In addition, the chemistry of the coating must be assessed if a match to the substrate can be realized. The use of interferometry, Rutherford backscattering, and x-ray photoelectron spectroscopy provide corresponding characterization of residual stress, the elemental composition, and the nature of chemical binding in the Si-O<sub>x</sub> coatings.

## Experimentals

The Si-O<sub>x</sub> coatings are sputter deposited using a planar magnetron operated in the rf mode. The 50.8 mm diameters targets are pure silicon and fused quartz, i.e. transparent vitreous silica. A forward target power of 250 Watts is used for each deposition. The source voltage is inferred from a bias potential as measured from the target. The working gas is an Ar-O<sub>2</sub> mixture that is flowed at a rate of 40 cc min<sup>-1</sup> and a pressure of 0.4 to 4.0 Pa. The oxygen partial pressure of the sputter gas mixture is controlled by flow rate and is generally held constant for each deposition experiment at 0.067 Pa. (The only exception is coating no. 403 wherein the oxygen partial pressure is 0.13 Pa.) For reference, the deposition system base pressure is 10<sup>-7</sup> Pa. The substrates are optically polished flats of fused quartz. The flats are right circular cylinders with a diameter of 25.4 mm and a thickness of 3.6 to 5.1 mm. The film thickness is measured using contact profilometry. A list of the gas pressure, target potential, coating thickness, and deposition rate for each sample are given in Table 1. Coatings no. 3xx and 4xx are deposited from the Si target whereas no. 6xx are deposited from the fused quartz target. Coatings that are up to 15 μm thick are produced for this study.

The residual stress in each coating is measured using a Fizeau Plano-Interferometer. The light source is a Helium-Neon laser with a characteristic wavelength ( $\lambda$ ) of 633 nm. A deflection in the surface of the optically flat substrate is created by the residual stress in the coating. For compressive stress the deflection of the surface is convex (upwards) and for tensile stress the deflection is concave (downwards). The height ( $h$ ) of the surface displacement is expressed as

$$h = 0.5 m \lambda \quad (1)$$

where  $m$  is the integral number of fringes produced in the interference pattern at a radius ( $r$ ) from the center of the coated substrate.

The elemental composition (at.%) of the Si-O<sub>x</sub> film is determined using Rutherford Backscattering (RBS). The computer program RUMP<sup>TM</sup> was used to interpret the results.<sup>[3]</sup> The films are analyzed using 2.3 MeV He<sup>+</sup> ions at normal incidence with a 2 mm x 2 mm beam spot at a 164° detection angle. Since the coatings are oxides, a relatively small current of 10<sup>-8</sup> amps is used to reduce charging. The absolute number of He<sup>+</sup> ions generating each spectrum was determined by a spinning-wire dosimetry system.<sup>[4]</sup> A fluence of 20 μCoulombs was measured during the exposure. The RBS spectra consist of unique signals for Si and O with a low background under the elemental signals. The intensity from each of the elements is determined with high precision and quantifiable through well known physical cross-sections.<sup>[3]</sup> The yield is normalized to the incident beam fluence and detector solid angle.

Electron spectroscopy for chemical analysis (ESCA) reveals the nature of chemical bonding. A Quantum 2000 Scanning ESCA Microprobe<sup>TM</sup> is used in this analysis. In the analysis of Si bonding within the Si-O<sub>x</sub> coatings, the use of angle-dependent x-ray photoelectron spectroscopy (XPS) provides a sensitive probe to determine the nature of bonding with depth. For analysis of these Si-O<sub>x</sub> coatings, a 45° angle is sufficient to reveal information about the bulk of the coating. A slot shaped aperture (3 mm x 10 mm) is used in front of the input lens to reduce the

acceptance angle and increase the angular resolution. The 2p binding energy of Si is 99.3 eV as measured using Al  $k\alpha$  radiation. The photoelectron line shifts for Si in SiO<sub>2</sub>, i.e. silica, to 103.3 eV. For the silanes (SiO) and silicates (Si-O<sub>x</sub> where 1 < x < 1.7), the 2p binding energy varies from 101.8 to 103 eV. The general concept regarding the shift is that the greater the electronegativity of the surrounding atoms, the displacement of electronic charge from the atom is more, and the observed binding energy is higher.

## Results and Analysis

The Si-O<sub>x</sub> coatings appear specular and transparent on the fused quartz substrates. A typical pattern produced from the interferometry measurements is shown (in Fig. 1) for coating no. 315. The interference pattern consists of concentric rings. Measurements of the number of interference fringes ( $m$ ) at a radius ( $r$ ) are then input to the analysis of residual stress as determined using the Brenner-Senderoff analysis <sup>[5]</sup> for thin films. The coating stress ( $\sigma$ ) is expressed as

$$\sigma = E_s [6(1-\nu_s)]^{-1} (t_s)^2 (t_f)^{-1} (R)^{-1} \quad (2)$$

where  $E_s$  is the elastic modulus of the substrate,  $\nu_s$  is the Poisson ratio of the substrate,  $t_f$  (the coating thickness) is much less than  $t_s$  (the substrate thickness), and  $R$  is the radius of curvature of the coating-substrate surface. The radius of curvature is equivalent to

$$R = (h^2 + r^2)(2h)^{-1} \quad (3)$$

In the context of the interferometry measurement,  $h$  is much less than  $r$ . Equation (3) simplifies to

$$R = (r^2)(2h)^{-1} \quad (4)$$

Substituting equation (1) into (4), and equation (4) into (2) yields the final expression for stress as

$$\sigma = E_s [6(1-\nu_s)]^{-1} (t_s)^2 (t_f)^{-1} (m\lambda) (r)^{-2} \quad (5)$$

The results for the computation of  $\sigma$  from equation (5) are plotted (in Fig. 2) as a function of the sputter gas pressure for coatings no. 3xx and 4xx as reactively sputter deposited from the pure Si targets, where it is assumed that  $E_s = 72.7$  GPa and  $v_s = 0.16$ . A local minimum in the compressive stress of -0.39 GPa (-81 ksi) appears at a gas pressure of 0.67 Pa for coating no. 315. The observation of a local minimum in compressive stress is an expected trend found in sputtered deposits.<sup>[6-8]</sup> The target potential and deposition rate (as listed in Table 1 for the 3xx and 4xx coatings) follow the same trend with sputter gas pressure as does the residual compressive stress (in Fig. 2).

The composition of the Si-O<sub>x</sub> coating is measured for two representative samples using RBS. Coating no. 412 is deposited from the Si target whereas coating no. 607 is deposited from the fused quartz target. The most significant difference between the deposition conditions of these two coatings is that the target voltage is an order of magnitude higher for coating no. 607. This may indicate that the sputtered species are more energetic. The RBS results are shown (in Fig. 3) where the normalized yield is plotted as a function of the backscattered ion energy. The best RUMP model fit is shown as a solid line and the data are shown as open circles (no. 412) and open triangles (no. 607). For the simulations, the actual detector resolution of 20 keV is used and the Bohr straggling is set as 1. This parameterization gives an excellent approximation to the theoretical limit to resolution. The simulated curves are shifted due to charging. Elemental content is determined by the step height at the corresponding channel. Step position is indicated for the elements found in the coatings. The chemical formula of coating no. 412 is modeled as K<sub>0.04</sub>Si<sub>1.00</sub>O<sub>2.00</sub> (or Ar<sub>0.04</sub>Si<sub>1.00</sub>O<sub>2.00</sub>) and that of coating no. 606 as Si<sub>1.00</sub>O<sub>2.00</sub>. Since the step height is constant from channel 360 to 270, i.e. an equivalent coating depth of 1  $\mu\text{m}$ , there is no indication of a change in composition from the deposited coating to the substrate.

The nature of the 2p chemical binding for Si in the Si-O<sub>x</sub> coating is measured for two representative samples using ESCA. Coating no. 403 is deposited from the Si target whereas coating no. 625 is deposited from the fused quartz target. As in the RBS analysis, the most significant difference between the deposition conditions of these two coatings is that the target voltage is an order of magnitude higher for coating no. 625. The ESCA surveys are shown for Si 2p (in Fig. 4) where the normalized intensity varies as a function of the binding energy. A Gaussian peak for both coating no. 403 (open circles) and no. 625 (open triangles) at 102.8 eV and 102.7 eV, respectively, indicates that there is just one single Si-O<sub>x</sub> phase (with  $x \sim 1.7$ ). This same peak position is produced from XPS of the fused quartz substrate as well.

## **Summary**

The reactive sputter deposition of silicon and fused quartz targets is used to produce stoichiometric SiO<sub>2</sub> coatings onto optically flat, fused quartz substrates. Interferometry is used to reveal that a minimum in the residual compressive stress of -0.4 GPa is found for an Ar-O<sub>2</sub> working gas pressure of 0.67 Pa. Characterization of the coating chemistry using RBS and XPS indicates that both the fused quartz and silicon targets can be used to sputter deposit coatings with the composition and chemical bonding features of the fused-quartz substrate material.

## **Acknowledgments**

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.



## References

1. D.R. Halfpenny and D.M. Kane, J. Appl. Phys., 86 (1999) 6641
2. D.M. Kane and D.R. Halfpenny, J. Appl. Phys., 87 (2000) 4548
3. RUMP program, Computer Graphics Service, Lansing, NY 14882, USA
4. R. G. Musket, R. S. Daley and R. G. Patterson, Nucl. Instr. and Meth., B83 (1993) 425
5. A. Brenner and S. Senderoff, J. Res. Natl. Bur. Stand., 42 (1949) 105
6. J. A. Thornton, J. Vac. Sci. Technol., 12 (1975) 830
7. J. A. Thornton, Annu. Rev. Mater. Sci., 7 (1977) 239
8. A. F. Jankowski, R. M. Bionta, and P.C. Gabriele, J. Vac. Sci. Technol. A, 7 (1989) 210

Table I. – The deposition parameters of the Si-O <sub>x</sub> coatings				
Sample Number	Working gas pressure (Pa)	Target potential (V)	Coating thickness (nm)	Deposition rate (nm min <sup>-1</sup> )
419	4.00	-110	189	0.35
403	2.66	-111	108	0.37
406	2.66	-120	185	0.55
417	2.00	-115	328	0.72
410	1.33	-132	223	1.12
315	0.67	-155	635	1.32
323	0.67	-147	130	1.08
412	0.40	-131	142	0.63
607	0.67	-1000	990	0.76
625	0.67	-1020	1040	0.80

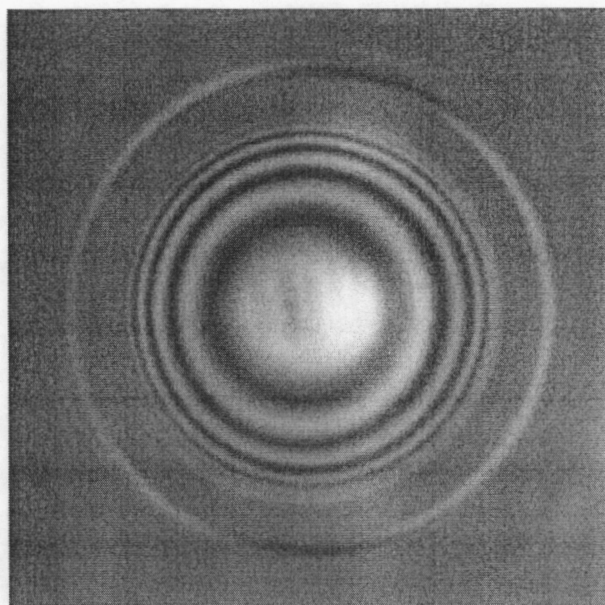


Figure 1 – An interference pattern produced by polarized light in Si-O<sub>x</sub> coating no. 315 on fused quartz.

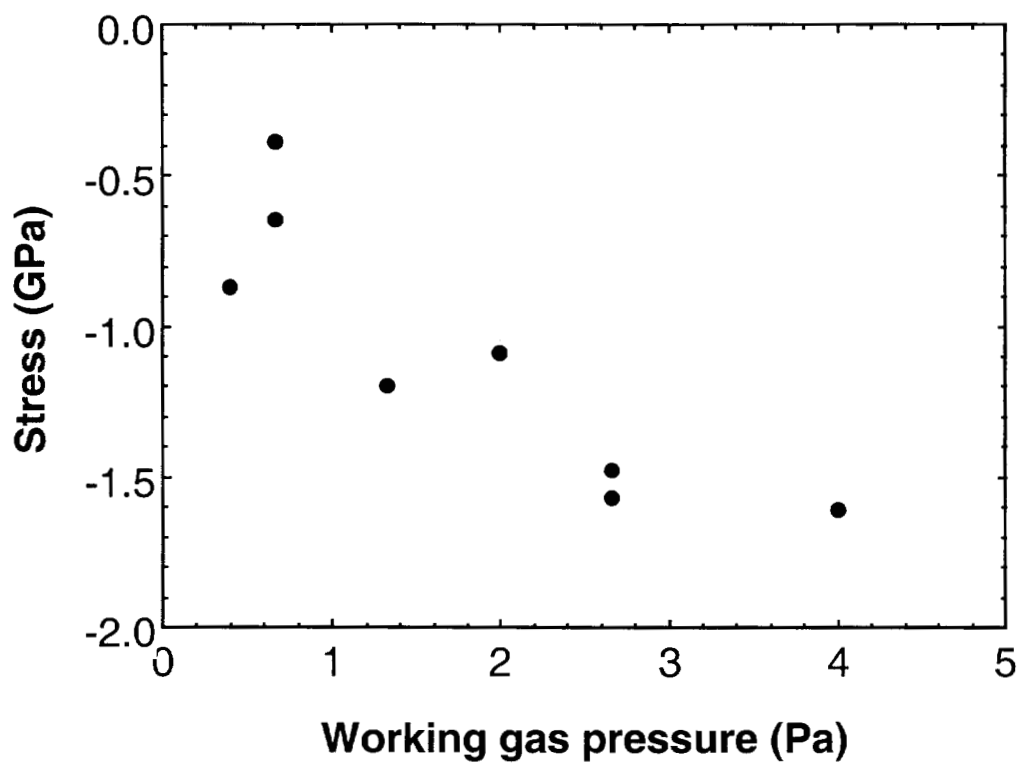


Figure 2. – The variation of residual stress (GPa) in the Si-O<sub>x</sub> coating reactively sputter deposited from a silicon target as function of the working gas pressure (Pa).

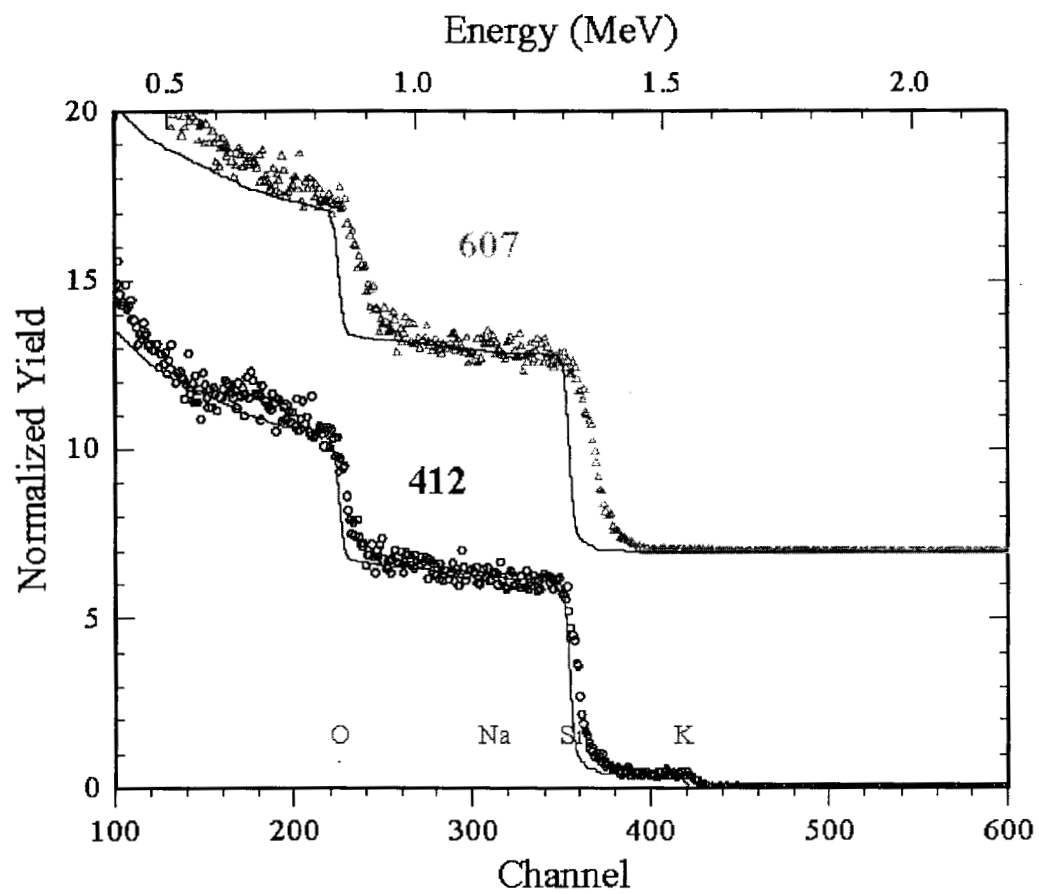


Figure 3. – The Rutherford backscattering measurements of ion yield from the Si-O<sub>x</sub> coatings no. 412 and no. 607. The yield is normalized to the incident beam fluence and detector solid angle.

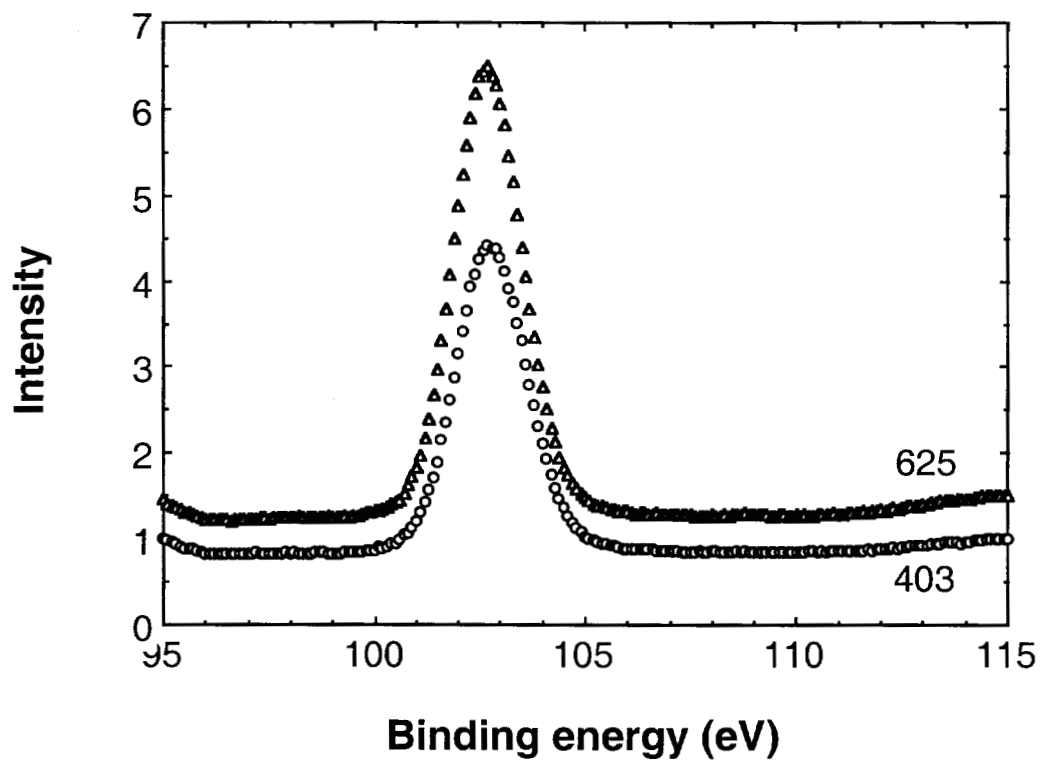


Figure 4 – The x-ray photoelectron spectra of the Si-O<sub>x</sub> coatings no. 403 and no. 625 as a function of the binding energy (eV).